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## FINAL TECHNICAL REPORT

# Synthesis of A Mesomorphic, Columnar Porphyrin for Fast Li Ion Conducting Electrolytes

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## 1. Introduction

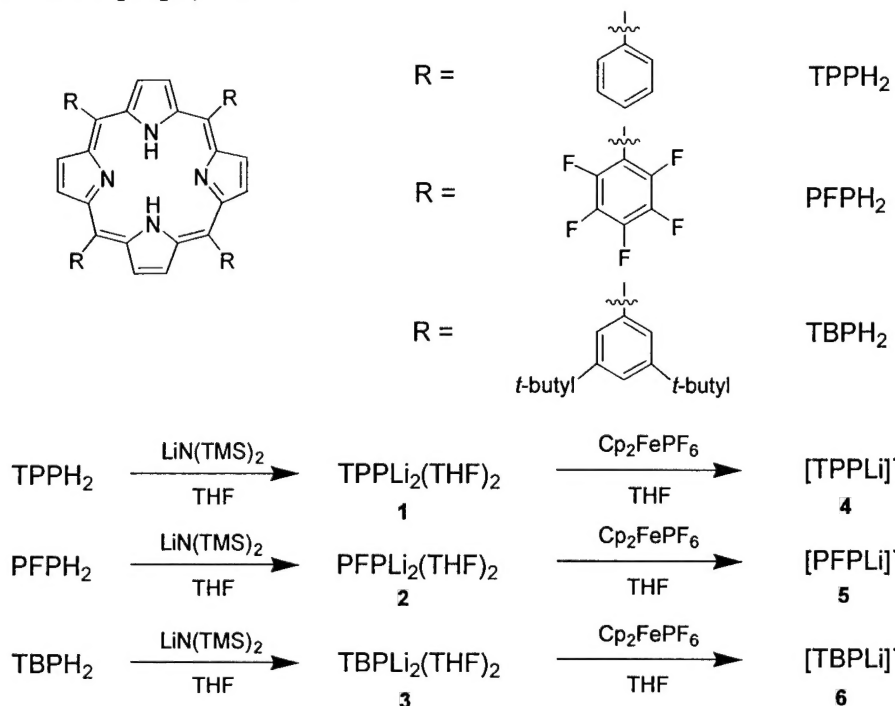
Most polymer electrolytes, which are usually oxygen-containing systems, rely on polymer segmental motion for ionic conduction. In general, ionic conduction in these electrolytes at ambient temperatures is poor. We proposed, in cooperation with Dr. Larry Scanlon and coworkers, to build and study a single ion conduction channel for lithium ions that eliminates the need for polymer segmental motion for ionic conduction. The basis of this design is to maintain a constant solvation sphere for the lithium ion within the channel and obtain a new class of polymer with a very low activation energy over a broad temperature range. In order to fabricate a single ion conducting channel for lithium ions, it is necessary to design a hollow tubular supermolecular structure by organization of the molecules into column stacks along the short axis of the molecules.

There are a number of examples of macrocyclic molecules that are good candidates for this purpose. Our original proposal focused on the functionalization of porphyrins to obtain liquid crystalline materials. The first generation of these materials has been synthesized and is currently under investigation in collaboration with Dr. Scanlon at Wright Patterson AFB. In the first stage this program, we focused on attempts to prepare a single ionconducting channel for lithium ions based on columnar mesomorphism, using synthetic strategies outlined in the proposal.

Our first efforts were aimed at molecular design and synthesis of a columnar, liquid-crystalline porphyrin, in which we hoped the conducting channels would be formed by the spine of the columnar stacks with a favorable face-to-face orientation. In more recent studies, we succeeded in preparing a monolithium radical anion that appears to show mesomorphic behavior and are continuing this work with the major short term goal of preparing enough material to conduct a full physical analysis. A limiting factor in this objective is the extreme air-sensitivity of the material which results from its paramagnetic character. Efforts to overcome this practical drawback are underway and, when successful, will have a significant impact on the program objective. Here we are investigating porphyrin ligands which, when deprotonated using our standard methodology, behave as mono-anionic ligands. The aim here is to retain the favorable characteristics of a one-dimensional porphyrin stack with lithium ions at the center, but to simplify the overall crystal packing problem by, in effect, removing the second exocyclic lithium. With only one possible covalent binding site, these complexes are predicted to possess only one lithium cation bound within the macrocyclic plane of the macrocycle. One has, therefore, not to consider the second lithium cation present in dianionic porphyrins, which needs to be solvated in some form both in the liquid and the solid state. Synthetic experience gathered with porphyrins led us to consider other macrocyclic systems for this purpose.

## 1. Research Summary

In the first stages of this work, two different approaches to the study of lithium complexes of porphyrins as fast lithium ion conducting polymers were taken. The first, classic system uses differently substituted porphyrins to study the effect of substituents on the geometry of the resulting complex (Scheme 1). A variety of different dilithioporphyrins (e.g. 1-3) have been prepared<sup>1</sup> and submitted for study to Dr. Larry Scanlon. Subsequently, these materials were oxidized using ferrocenium hexafluorophosphate. This produces the neutral  $\pi$ -radical porphyrins 4-6.



Scheme 1

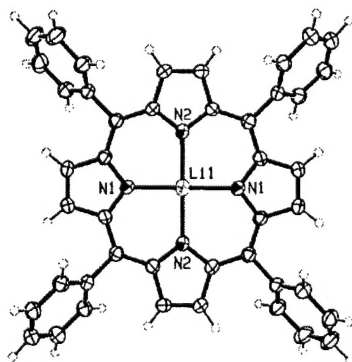
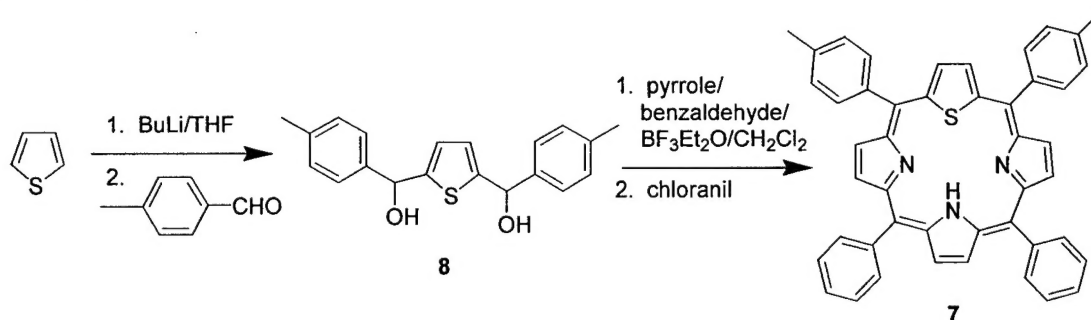


Figure 1

The second approach to lithiated porphyrin ligands involves the synthesis of mono-anionic porphyrin ligands, which possess a simpler coordination environment. That is because only one possible covalent binding site is left, and thus these complexes are expected to possess only one lithium cation bound within the macrocyclic plane of the macrocycle. One has, therefore, not to consider the second lithium cation present in

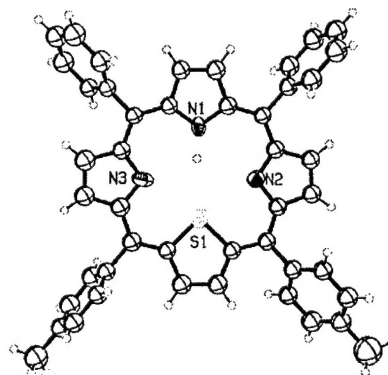
Proton NMR spectroscopy showed compounds 4-6 to be NMR silent, which was the first indication for the formation of a paramagnetic species. This was then confirmed by EPR spectroscopy, which showed all materials to be organic radicals with g-values at 2.00. A solid state X-ray crystallographic analysis of  $[\text{TPPLi}]^+$  4 (Figure 1) confirmed that this compound possesses one centrally bound lithium atom, which is bound to nitrogen atoms 1 and 2 with distances of ca. 2.04 and 2.07 Å, respectively.

dianionic porphyrins, which needs to be solvated in some form both in the liquid and the solid state.

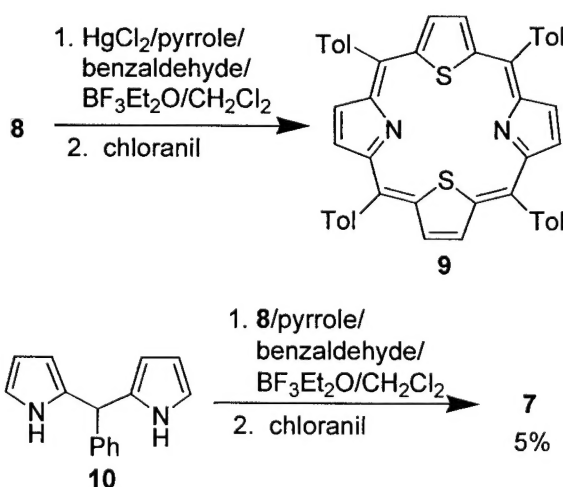


**Scheme 2**

The major focus of our synthetic work has been placed on the development of a reasonably easy and high yielding procedure to synthesize monoanionic porphyrins. Synthetic efforts focused on the monothiaporphyrin **7**. This material (albeit  $\beta$ - and not *meso*-substituted) was first reported by Broadhurst *et al.* in 1971.<sup>2</sup> Latos-Grazynski and coworkers later reported the syntheses of tetraphenyl monothiaporphyrin.<sup>3,4</sup> Compound **7** has been successfully synthesized in our laboratories following the synthetic route outlined in Scheme 2. This procedure involves the reaction of thiophene with 2.1 equivalents of *n*-butyl lithium, followed by the addition of excess *p*-tolylaldehyde. This results in the thiophene dialcohol **8**, which is then condensed with pyrrole and benzaldehyde to form, after oxidation with chloranil, the desired monothiaporphyrin **7**. This material was subsequently characterized in the solid state using X-ray crystallography (Figure 2).



**Figure 2**

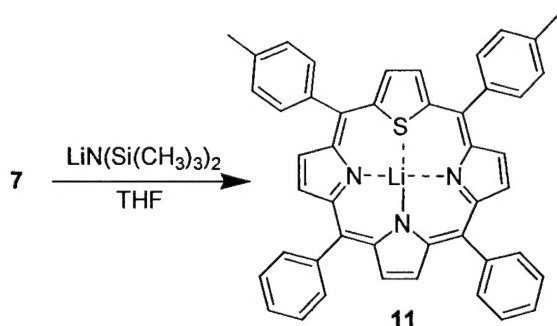


**Scheme 3**

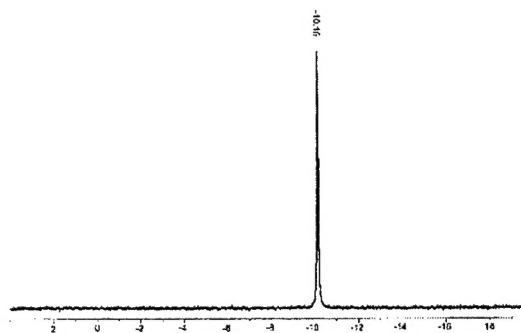
Using the above reaction sequence, monothiaporphyrin **7** can be obtained in only about 8% yield. Thus, major synthetic efforts were focused on the development of higher yielding synthetic procedures. The first attempt to prepare **7** *via* template effect by adding mercury(II)chloride to the reaction mixture led to the formation of the dithiaporphyrin **9** almost exclusively (Scheme 3). Similarly, the dipyrromethane **10** was prepared and condensed with the dialcohol **8**, following literature procedures describing a more efficient synthesis of monooxaporphyrin. However, this procedure also did not lead to higher yields of monothiaporphyrin **7**.

Monothiaporphyrin **7** was then lithiated using 1.2 equiv. of lithium bis(trimethylsilyl)amide (Scheme 4). This produces the monolithiated porphyrin **11**. NMR

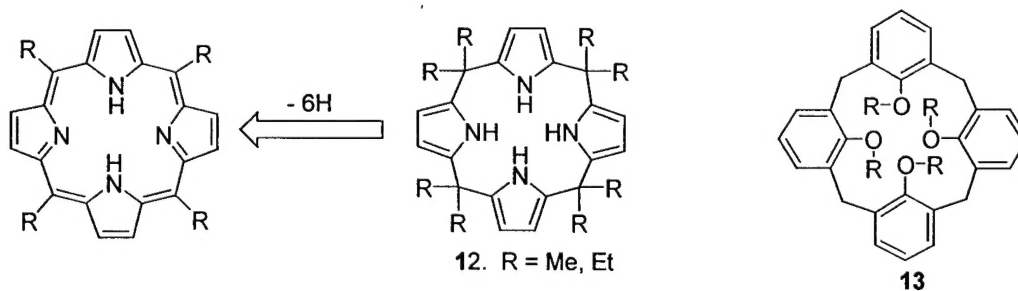
spectroscopic studies indicate that the lithium atom is bound centrally within the macrocyclic plane. This is based on: (a) the absence of a proton signal at high field assignable to the internal NH, and (b) the shift of the lithium signal in  $^7\text{Li}$  NMR to  $-10.15$  ppm (see Figure 3), a chemical shift usually observed for the internally bound lithium dilithioporphyryr samples at low temperatures. Conductivity properties of this material are currently under investigation.



Scheme 4

Figure 3.  $^7\text{Li}$  NMR of **11** in  $\text{C}_6\text{D}_6$ .

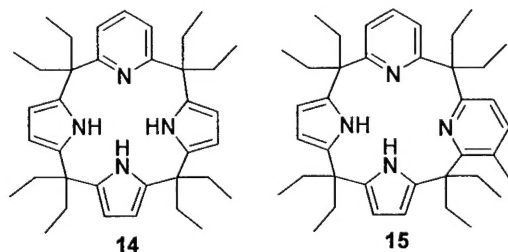
The work described above has shown that, while porphyrins are accessible and display desirable stacking behavior in the solid state, they are not the ideal set of macrocycles to pursue this type of chemistry. Primarily this is due to their low yielding synthesis, especially once unsymmetrical macrocycles are prepared. Thus, in the latter stages of this work, our focus shifted to a different class of macrocyclic compound, closely related to the porphyrins, the porphyrinogens or calixpyrroles.<sup>5-7</sup>



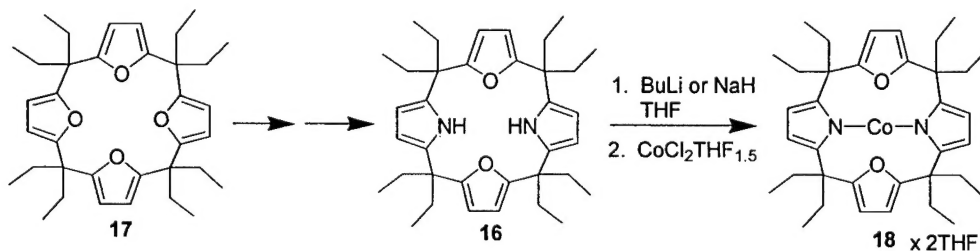
Calix[4]pyrroles, **12**, have been known for more than 100 years, and are synthesized by the acid catalyzed condensation between pyrrole and a ketone such as acetone.<sup>8</sup> This prototypical macrocycle has been studied mainly under the aspect of being an analogue to the naturally occurring tetrapyrrolic intermediates in the biosynthesis of porphyrin.<sup>5-7</sup> For this reason these materials are frequently referred to as porphyrinogens, although here we will use the term calix[4]pyrrole.<sup>9,10.\*1</sup>

\*1 This is because i) it possesses four *bis*-alkyl substituted,  $\text{sp}^3$  hybridized *meso* carbons which prevent it from being oxidized to the porphyrin, and ii) it possesses structural similarity to calixarenes (e.g. **13**).<sup>11</sup>

The ability of calix[4]pyrrole to coordinate metals has been studied extensively. Complexes with Zr(IV), Ti(IV), V(V), Mo(VI), W(VI), Nb(V), Pr(III), and Nd(III) have been prepared *via* metathesis reactions between their alkali salts and the respective metal halides.<sup>5,7</sup> These studies revealed that calix[4]pyrroles display different binding modes, with each pyrrolyl anion being able to bind in  $\eta^1$ ,  $\eta^3$ , or  $\eta^5$  fashion, thus providing 2, 4 or 6 electrons, respectively, to a metal. They were found to stabilize high metal oxidation states *via* a peculiar redox system that involves, among other things, the formation of cyclopropane subunits that serve as two electron shuttles.<sup>6</sup> The derived metal-calix[4]pyrrole complexes were also found to be able to bind and transport metal ions, specifically alkali cations, through their electron rich periphery.<sup>5,7,12</sup> These properties make this type of macrocycle a very interesting candidate for the application as fast lithium ion conducting electrolyte.



Very little work has been done with calix[4]pyrroles containing less than four anionic binding sites. One example of such calix[4]pyrroles are mixed pyrrole-pyridine macrocycles.<sup>5</sup> Prepared by ring expansion of calix[4]pyrrole, this produced calix[1]pyridine[3]pyrrole **14**, and upon further reaction calix[2]pyridine[2]pyrrole **15**. These materials were found to form complexes with titanium(IV), (in the case of **14**) and vanadium(III) (in the case of **15**). Additionally, **14** forms bimetallic complexes between lithium and the transition metals Fe(II), Co(II), Ni(II), and Cu(II). When submitted to oxidation, these materials were found to form C-C bonds both intra- or intramolecularly.

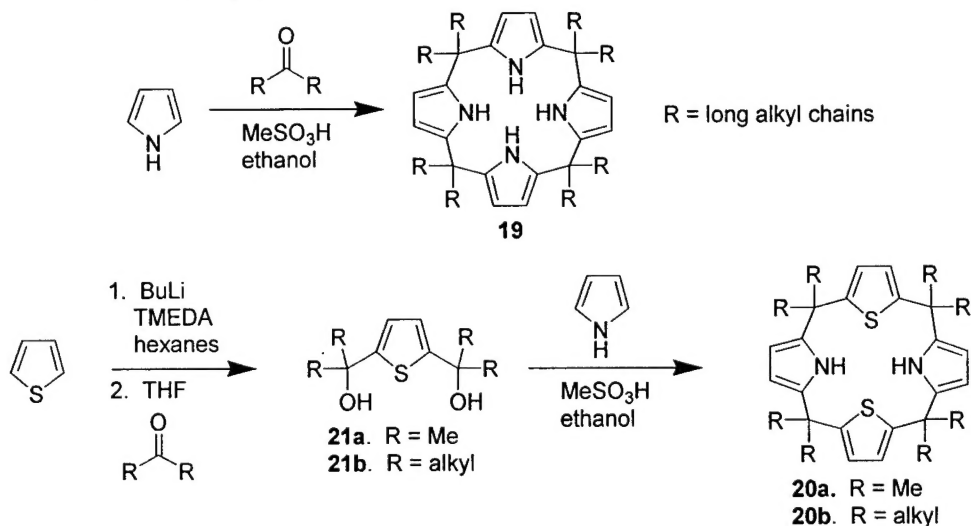


Scheme 5

Another way to synthesize calix[4]pyrrole ligands with less than four coordination sites is to introduce heteroatoms other than nitrogen into the ring system. One example for this type of macrocycle, the N<sub>2</sub>O<sub>2</sub> calix[2]pyrrole[2]furan (**16**), has been prepared by Floriani and coworkers from calix[4]furan, **17** (Scheme 5).<sup>13</sup> This material was found to coordinate Co(II) in the center of the macrocycle, **18**. However, no further details about the properties of this macrocycle, or that of other metal complexes, have been forthcoming.

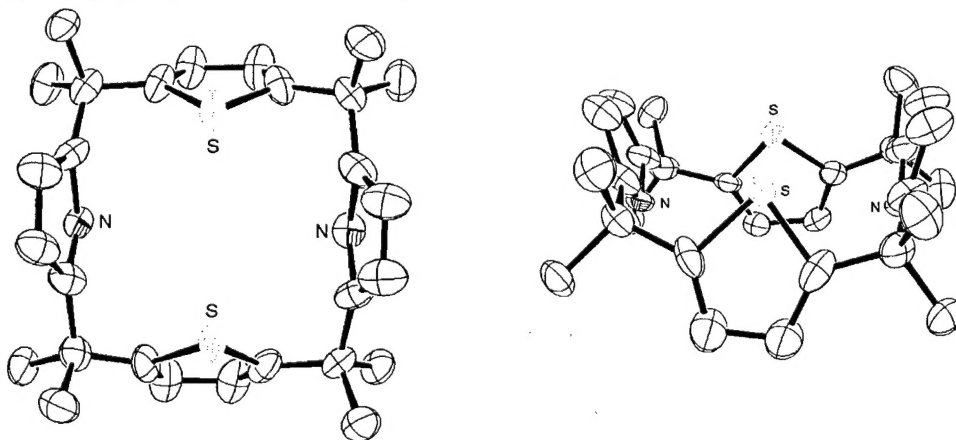
Two types of easily prepared and functionalized macrocycles were investigated. The first is calix[4]pyrrole **19** and its derivatives, which were prepared according to literature procedures using pyrrole and the appropriate ketone. The second is calix[2]pyrrole[2]thiophene, **20**. While calix[4]pyrroles are not planar in solution and the

solid state (*vide infra*), the liquid crystallinity can be introduced through the *meso*- or  $\beta$ -positions on the macrocycle.



**Scheme 6**

A prototypical  $N_2S_2$  calix[2]pyrrole[2]thiophene, the *meso*-octamethyl dithiacalix[4]pyrrole **20a**, has been prepared. This compound was synthesized by reacting dilithiothiophene,<sup>14</sup> formed *in situ*, with an excess of acetone. The product, bis(dimethylhydroxy)methyl thiophene **21**, was then reacted with one equivalents of pyrrole in ethanol using methane sulfonic acid as catalyst. This leads to the  $N_2S_2$  calix[2]pyrrole[2]thiophene **20a** in 50% yield.



**Figure 4.** Front (left) and side (right) views of the solid state structure of  $N_2S_2$  calix[2]pyrrole[2]-thiophene **20a**.

The macrocycle **20a** was, among other things, characterized in the solid state using single crystal X-ray crystallography (Figure 4). The solid state structure revealed that the  $N_2S_2$  calix[2]pyrrole[2]thiophene adopts the typical 1,3-alternate conformation (i.e., adjacent pyrrole and thiophene moieties are oriented in opposite directions) observed for essentially all structurally characterized calix[4]pyrroles. It also shows that these materials possess a well-defined binding pocket where the coordination of two lithium cations can take place.

The above preparation procedure can easily be extended to generate a wide variety of differently substituted  $N_2S_2$  calix[2]pyrrole[2]thiophenes. This can be done by either



modifying the pyrrolic and/or thiophenic  $\beta$ -positions or through introduction of different *meso*-substituents. Initial studies will, for reasons of simplicity, focus on the latter.

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Gebauer, A.; Dawson, D.Y.; Arnold, J. "Neutral  $\pi$ -radicals of lithium porphyrins: synthesis and characterization" *J. Chem. Soc., Dalton Transactions*, **2000**, 111-112.

Arnold, J. "Alkali Metal Porphyrins" in *"The Porphyrin Handbook"* Guillard, R., Kadish, K.M., Smith, K. Eds, 1999, Ch 17.

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